Appendix G
Calculations

Appendix G. Calculations

Section I. Material Balance

1. Purpose: To calculate a mass balance for the combustion of chemical agent HD in cut away TCs in the MPF at the CAMDS Site.

2. Assumptions:

a. Only the liquid portions of agent HD are to be treated in the MPF.

b. The maximum amount of agent HD is 109 lbs per charge to the MPF. The charge interval is 80 minutes.

c. The composition data (Tables G-1 and G-2) are average values from the preliminary sampling results of HD TCs at DCD.

d. Natural gas (CH_4) consumption and stack air data were calculated previously for GB heels in the MPF; *Metal Parts Furnace Performance Standard Demonstration Burn Using Ton Containers With Agent GB Heels, Volume 1*, 12 October 1995.

e. Combustion values in both the PCC and SCC are included in the estimate.

Table G-1. HD Composition—Organic Compounds

Organic Compound	Chemical Formula	Percent by weight
Bis(2-chloroethyl)sulfide	$C_4H_8Cl_2S$	89.1%
1,2-Dichloroethane	$C_2H_4Cl_2$	0.64%
Q-Mustard	$C_6H_{12}Cl_2S_2$	3.21%
T-Mustard	$C_8H_{16}OCl_2S_2$	0.17%
Hexachloroethane	C_2Cl_6	0.2%
Note: other organic compounds present in trace amounts (i.e., ppm) were ignored. Other non-combustible (inert) materials were not included.		

Table G-2. HD Composition—Metals

Metal	Concentration (mg/kg)
Al	39
Sb	5.1
As	6.97
Ba	5.56
Be	5.18
B	9.45
Cd	5.18
Cr	4.72
Co	1.03
Cu	37.3
Pb	4.75
Mn	1.75
Hg	4.34
Ni	3.29
Se	10
Ag	5.2
Tl	5.2
Sn	10.4
V	3.16
Zn	9.86

3. Calculations.

a. Natural Gas (CH_4) Consumption: Beginning with an average CH_4 flow rate of 5100 standard cubic feet per minute (scfm) during runs 4, 5 and 6, we converted scfm to lbs/hr, assuming standard conditions of 77° F (536.67° Rankine(R)] and 1 atmosphere (atm).

$$n = \frac{PV}{RT} = \frac{(1atm)\left(5100\,\frac{ft^3}{hr}\right)}{\frac{0.7302\,ft^3 - atm}{(lb-mol)(^{o}R)}\left(536.67^{o}R\right)} = 13.01\,\frac{lbmol}{hr}$$

The mass feed rate of CH_4 is

$$13.01\,\frac{lbmol}{hr}\left(16.04\,\frac{lb\ CH_4}{lbmol\ CH_4}\right) = 208.7\,\frac{lb\ CH_4}{hr}$$

b. Balanced Combustion Reaction Equations

HD Mustard ($C_4H_8Cl_2S$)

$$C_4H_8Cl_2S + 6.5\ O_2 \rightarrow 4CO_2 + SO_2 + 2\ HCl + 3\ H_2O$$

1,2-Dichloroethane

$$C_2H_4Cl_2 + 2.5\ O_2 \rightarrow 2\ CO_2 + 2\ HCl + H_2O$$

Q-Mustard

$$C_6H_{12}Cl_2S_2 + 10.5\ O_2 \rightarrow 6\ CO_2 + 2\ HCl + 5\ H_2O + 2\ SO_2$$

T-Mustard

$$C_8H_{16}OCl_2S_2 + 13O_2 \rightarrow 8\ CO_2 + 2\ HCl + 7\ H_2O + 2\ SO_2$$

Hexachloroethane

$$C_2Cl_6 + \tfrac{1}{2}\ O_2 + 3H_2O \rightarrow 2\ CO_2 + 6\ HCl$$

c. Calculation of Dry Combustion Air Feed. The feed rate of air through the combustion chambers is estimated from the stack gas data from the October 1995 report of Performance Test of GB agent heels, runs 4, 5, and 6 in the MPF:

Average Stack Moisture Content	38.1% (volume basis)
Average Stack CO_2 Concentration	4.3% (dry basis)
Average Stack CO Concentration	8 ppm
Average Stack O_2 Concentration	13.3% (dry basis)
Average Stack Gas Temperature	230° F, [689.67° R]
Average Stack Gas Flow	5,010 (scfm, wet) from PAS data, Table 5-1 (average of runs 4-6).
Standard conditions are	77° F (536.67° R), and 1 atm.

The dry stack gas flow rate = (1.0 - 0.381) (5,010) = 3101.19 scfm

The dry stack gas molar feed rate is calculated from the ideal gas law:

$$n=\frac{PV}{RT}=\frac{(1atm)\left(3101.19\frac{ft^3}{\min}\right)}{\frac{0.7302 ft^3-atm}{(lb-mol)(^\circ R)}(537.67\ ^\circ R)}=7.9\frac{lbmol}{\min}\left(\frac{60\min}{hr}\right)=473.94\frac{lbmol}{hr}$$

The dry stack gas consists primarily of nitrogen, oxygen, and carbon dioxide. Trace amounts of carbon monoxide, chlorine, oxides of sulfur and nitrogen also are present in levels measured in ppm; however, the gas species present in trace amounts are ignored to simplify the calculation. The estimated molar fraction of nitrogen in the stack gas is:

100% - 13.3% (O_2) - 4.3% (CO_2) = 82.4% N_2

The molar feed rate of nitrogen is

0.824 N_2 × (474.05 lbmol/hr) = 390.53 lbmol N_2 / hr

$$\text{feed rate of dry air}=\frac{390.53\frac{\text{lbmol}}{\text{hr}}}{0.79}=494.33\frac{lbmol}{hr}\left(\frac{29lbs}{lbmol\ air}\right)=14{,}335\frac{lbs}{hr}$$

The calculated values for combustion air, natural gas, and the feed composition data were entered into the material balance spreadsheet (Figure G-1). The resulting combustion gases are provided in Table G-3 below.

Table G-3. Combustion Gas Production Rates

Gas Species	Production (lb-mols/hr)	Production (lbs/hr)
CO_2	14.90	656
H_20	27.44	494
N_2	392.40	10,987
HCl	0.94	34.5
SO_2	0.48	30.5
O_2	75.3	2408.8

The metals present in agent HD will be partitioned between the stack gas, ash stream, and the scrubber brines. The metals feed rates (grams per hr) are given in the material balance spreadsheet, Figure G-1.

d. Heat of Combustion. The high heating value of agent HD is 8,500 British Thermal Units (btu) per lb (Reference CAMDS part B permit, Attachment 2, pg. 35). The total heat input per hour is estimated as 5.67 M btu/hr (Table C-5), according to:

$$\left(109\left(\frac{60}{80}\right)\frac{lbs\ HD}{hr} \times 8500\frac{btu}{lb} + 208.7\frac{lbs\ CH_4}{hr} \times 23{,}861\frac{btu}{lb}\right) = 5.67 \times 10^6\ \frac{btu}{hr}$$

4. Discussion.

a. Excess air was included in the analysis of combustion air feed rates.

b. The combustion air feed was assumed to be the same as that used during the GB Heel performance test using a 109-lb charge of GB. Agent GB has a heating value 18.5% higher than HD. The routine treatment of GB in cut-away TCs in the MPF suggests that HD can be successfully treated in the MPF.

COMBUSTION WORKSHEET HD COMPLIANCE TEST changes

HD Charge wt.[lbs] 109 Charge interval [redacted] (minutes)

Feed Compounds	Compound Formula	Weight (lb/hr fed)	C	H	O	N	Cl	F	S	Compound Mol Wt	Lbmols of feed compound	mol percent	HD Specie
HD (Mustard)	$C_4H_8Cl_2S$	72.83925	4	8			2		1	159.06	0.457924169	0.000897435	C4H8Cl2S
1,2-Dichloroethane	$C_2H_4Cl_2$	0.522383	2	4			2			98.95	0.00527915	1.0346E-05	C2H4Cl2
Q-Mustard	$C_6H_{12}Cl_2S_2$	2.624175	6	12			2		2	219.18	0.011972912	2.34644E-05	C6H12Cl2S2
T-Mustard	$C_8H_{16}OCl_2S_2$	0.138975	8	16	1		2		2	263.23	0.000527964	1.0347E-06	C8H16OCl2S2
Hexchloroethane	C_2Cl_6	0.1635	2				6			236.72	0.000690689	1.35361E-06	C2Cl6
Nat Gas	CH_4	[redacted]	1	4						16.04	13.0095998	0.025496069	
Dry Air	n/a												(HD compounds
O_2	O_2	3340.055			2					32.00	104.3767188	0.204556335	
N_2	N_2	10994.95				2				28.02	392.3963241	0.769013962	
Totals ✦		14619.99	14.92929734	55.88	208.8	785	0.956	0	0.48		510.2590375	1	
		lbs.	← Total Element lb mols, monatomic →										

	Combustion Gas Species Formed						
	CO2	H2O	N2	HCl	SO2	HF	O2
No. mols	14.92929734	27.46	392.4	0.96	0.483	0	75.23
Molec. Wt.	44	18	28	36.5	64	20	32.00
Weight [lbs/hr]	656.8890831	494.3	10987	34.9	30.91	0	2407.52

Metal	Conc. [ppm]	Metal Feed (grams/hr)	
Al	39	1.45E+00	1
Sb	[redacted]	1.89E-01	2
As	6.97	2.58E-01	3
Ba	5.56	2.06E-01	4
Be	5.18	1.92E-01	5
B	9.45	3.50E-01	6
Cd	5.18	1.92E-01	7
Cr	4.72	1.75E-01	8
Co	1.03	3.82E-02	9
Cu	37.3	1.38E+00	10
Pb	4.75	1.76E-01	11
Mn	1.75	6.49E-02	12
Hg	4.34	1.61E-01	13
Ni	3.29	1.22E-01	14
Se	10	3.71E-01	15
Ag	5.2	1.93E-01	16
Tl	[redacted]	1.93E-01	17
Sn	10.4	3.86E-01	18
V	3.16	1.17E-01	19
Zn	9.86	0.365618487	20

Figure G-1. Material Balance Spreadsheet

Section II. Calculation of Flow and Emission Rates

1. Basis for Calculations.

a. Stack flow = 5,010 standard cubic feet per minute (scfm) = 300,600 standard cubic feet per hour (scfh) at standard conditions of 68° F, 1 Atmosphere (Atm).

b. Stack moisture = 38 volume or molar percent.

c. Stack O_2 = 13.5%.

d. Flow Calculation [from wet scfh to dry standard cubic meters per hour (dscmh) @ 7% O_2]:

$$300{,}600\ std\ {}^{ft^3}\!/_{hr} \times (1-0.38)\left(\frac{20.9-13.5}{20.9-7}\right)\left(\frac{0.02832\,m^3}{ft^3}\right) = 2809.9\,dscmh^*$$

*rounded up to 2810 dscmh

2. Projected Emission Rates. The projected emission rates are calculated in the spreadsheet *MPF_Metals_Emissions.XLS*, and provided in Figure G-2. Included are removal efficiency data from similarly equipped incinerators. The chosen removal efficiencies are shown in the shaded cells. The removal efficiency data are provided in Table G-3, page G-9.

Table C-10, HD Metals Removal Efficiencies

new changes, or checked

Projected Emission Rates of HRA Metals

MPF flow rate *5010* *[scfm]* *stack O_2 (percent)* 13.3 *stack moisture [vol %]* 0.38

Charge Weight 109

Metal	Feed (gm/hr)	RE (%)	RE source	Em. Rate (gm/sec)	Conc.[µg/dscm @7%O2]	Projected Em. Rate (gm/hr)	Screening Limit[1] (gm/hr)
Al	1.446158318	99.59	D	1.64701E-06	2.04576	5.92925E-03	
Sb	0.189113011	99.75	B	1.31328E-07	0.16312	4.72783E-04	1.40E+01
As	0.258454448	99.45	A	3.94861E-07	0.49046	1.42150E-03	1.10E-01
Ba	0.206170263	99.96	E	2.29078E-08	0.02845	8.24681E-05	2.40E+03
Be	0.192079489	98.782	F	6.49869E-07	0.80720	2.33953E-03	2.00E-01
B	0.350415285	99.87	D	1.26539E-07	0.15717	4.55540E-04	
Cd	0.192079489	99.44	A	2.98790E-07	0.37113	1.07565E-03	2.60E-01
Cr	0.175022237	99.39	B	2.96565E-07	0.36837	1.06764E-03	4.00E-01
Co	0.038193412	97.26	D	2.90694E-07	0.36107	1.04650E-03	
Cu	1.383120647	99.96	D	1.53680E-07	0.19089	5.53248E-04	
Pb	0.176134667	99.15	B	4.15874E-07	0.51656	1.49714E-03	4.30E+00
Mn	0.064891719	92.66	B	1.32307E-06	1.64339	4.76305E-03	
Hg	0.160931464	0	n/a	4.47032E-05	55.52600	1.60931E-01	1.40E+01
Ni	0.121996432	99.12	B	2.98214E-07	0.37041	1.07357E-03	
Se	0.370809825	99.63	D	3.81110E-07	0.47338	1.37200E-03	
Ag	0.192821109	99.66	D	1.82109E-07	0.22620	6.55592E-04	1.40E+02
Tl	0.192821109	99.41	A	3.16012E-07	0.39252	1.13764E-03	1.40E+01
Sn	0.385642218	99.99	D	1.07123E-08	0.01331	3.85642E-05	
V	0.117175905	85.28	D	4.79119E-06	5.95116	1.72483E-02	
Zn	0.365618487	98.782	F	1.23701E-06	1.53649	4.45323E-03	

	Metal	Conc. In HD [mg/Kg]	Metal wt / charge [gm]
1	Al	39	1.92821109
2	Sb	5.1	0.252150681
3	As	6.97	0.344605931
4	Ba	5.56	0.274893684
5	Be	5.18	0.256105986
6	B	9.45	0.46722038
7	Cd	5.18	0.256105986
8	Cr	4.72	0.233362983
9	Co	1.03	0.050924549
10	Cu	37.3	1.844160863
11	Pb	4.75	0.234846223
12	Mn	1.75	0.086522293
13	Hg	4.34	0.214575285
14	Ni	3.29	0.16266191
15	Se	10	0.4944131
16	Ag	5.2	0.257094812
17	Tl	5.2	0.257094812
18	Sn	10.4	0.514189624
19	V	3.16	0.15623454
20	Zn	9.86	0.487491317

1. Tier II emissions screeing limits, urban and rural, complex terrain, stack height 4 meters.

MACT Metals Emissions

	Metal(s)	Projected Conc. [µg/dscm]	MACT Limit [µg/dscm]
semi vol	Pb, Cd	0.89	240
low vol	As, Be, Cr	1.67	97
volatile	Hg	55.53	130

Source of Removal Efficiencies

A. UMDA, mini-burn #1, hi metals feed
B. UMDA, mini-burn #2, lo metals feed (85% reduction from mini-burn #1)
C. ANCDF, surrogate TB
D. TOCDF, MPF TB, worst runs
E. JACADS, SRA report
F. EPA spreadsheet, incinerators, SRE of LVM, June 02, (Ausimont facility, TB)

Figure G-2. Metal Emissions Spreadsheet.

Table G-3. Metal Removal Efficiency From Test Data(1)(2)

Metal	UMDA Mini-burn #1 Hi Metals Feed	UMDA(3) Mini-burn #2, Lo Metals Feed	ANCDF, Surrogate TB	TOCDF MPF TB (worst runs)	JACADS SRA report	EPA(4) Spreadsheet
Al				99.59		
Sb	99.76	99.75	99.83	99.75		
As	99.45	99.65	99.65	99.52		
Ba				99.99	99.96	
Be				69.24		98.782
B				99.87		
Cd	99.44	99.48	99.65	99.99	99.98	
Cr	99.77	99.39	99.57	99.99	99.95	
Co				97.27		
Cu				99.96		
Pb	99.32	99.15	99.64	99.99	99.97	
Mn	99.47	92.66	99.56	24.24*		98.782
Hg	99.42	99.18	99.43	n/a		
Ni	99.43	99.12	99.57	99.99	99.96	
Se	99.87	99.86	99.96	99.62		
Ag				99.66		
Tl	99.41	99.59	99.77	99.87		
V				85.28		
Zn				99.99		98.782

(1) Values set at detection limits.
(2) Efficiencies chosen for this study are shaded.
(3) 85% reduction from UMDA Mini-burn #1.
(4) From Incinerators, SRE of LVM, June 02, Ausimont facility, TB.
Note: The chosen removal efficiencies are shown in the shaded cells.

Section III. Residence Gas Time in the Secondary Combustion Chamber

1. **Purpose**: Estimate the MPF gas residence time in the SCC.

2. **Assumptions:**

   a. The standard gas flow conditions are 1 atm and 68° F.

   b. Ambient air humidity during testing is 10% relative humidity (July is normally dry); ambient temperature is 90° F.

   c. No gas in-leakage exists between the SCC exit and the Stack.

d. Ambient atmospheric pressure at stack is 12.3 psia, corresponding to 5000-ft elevation.

3. Data. All data are from the 1995 MPF test burn report (average of runs 4 to 6) that used TCs with GB agent heels.

a. SCC total volume = 683 ft^3

b. Average Stack gas flow rate = 5,100 scfm

c. Average SCC draft = 5.97 iwc

d. Average SCC zone 1 temperature = 1653° F

e. Average SCC temperature = 1664° F

f. Average SCC zone 2 temperature = 1675° F

g. Average Stack gas temperature = 225° F

h. Average Stack gas moisture = 38.1 percent volume

4. Calculations.

a. Volume correction for water vapor added downstream of SCC for air at 90° F, 1 atm, 10% RH, humidity is 0.003 lb water / lb dry air from McCabe & Smith *Unit Operations of Chemical Engineering, 3rd. Ed.* page 748. The volume percent of water is calculated using the correction:

$$\frac{(0.003\,lb\,H_2O / 18.01\,lb/mol)}{1\,lb\,air / 29\,lb/mol} = 0.0048\,\frac{mol\ water}{mol\ dry\ air} = 0.0048\ volume\ \%\ water\ in\ ambient\ air$$

b. The volume of water added downstream of SCC is equal to the Average Stack gas moisture minus the correction:

38.1 volume percent - 0.0048 volume percent = 38.09 percent by volume

c. The correction of wet stack gas at standard conditions to actual conditions in the SCC uses the ideal gas law times the volume percent correction:

$$\frac{(0.003\,lb\,H_2O / 18.01\,lb/mol)}{12.3-(5.64\,iwc/27.2\,iwc/psi)} \times \frac{1490+459.67}{68+459.67} \times (1-0.381) = 3.031917144$$

d. The actual volumetric flow rate through the SCC is equal to the stack flow rate (wet, scfm) times the correction factor:

5,100 scfm X 3.031917144 = 15,462.78 dry acfm

e. The gas residence time in the SCC is equal to the SCC volume (ft^3) divided by the gas flow rate (ft^3/min), and converted from minutes to seconds:

683 ft^3 ÷ 15,462.78 dry acfm x 60 sec/min = 2.65 seconds

Section IV. POHC Destruction and Removal Efficiency (DRE) Calculations

1. Purpose. The purpose of this section is to confirm that 99.99% DRE for Agent HD can be validated using the proposed methods and sampling times. The POHC to be sampled is Mustard Agent HD.

2. Data Collection. The MPF stack gas will be sampled using DAAMS solid sorbent sampling tubes. The detection limit is 0.2 of the allowable stack concentration (ASC) level of 360 ng of agent, or 72 ng.

a. Stack sampling time is 240 minutes

b. Stack sampling flow rate is 0.15 L/min

3. Assumptions.

a. The lowest amount of HD agent that will be fed during the Trial Burn is 34 lbs per charge, or 34 lbs x 60 minutes/hour ÷ 80 minutes/charge = 25.5 lbs HD per hour.

b. A DRE of 99.99 percent will be achieved.

c. Average stack gas flow rate = 5010 scfm (wet).

d. Average stack gas temperature = 230 °F.

4. Calculations.

a. Flue Gas Mass Flow. At 99.99% DRE, the stack gas mass flow rate of HD will be:

$$25.5\frac{lbs}{hr}\times\left(1-\frac{99.99}{1000}\right) \quad = \quad 0.00255\frac{lbs}{hr}$$

b. Wet actual stack flow is:

$$5010\frac{ft^3}{\min}\times\frac{(230+459.67^{o}F)}{(77+459.67^{o}F)}\times\frac{14.696psi}{12.3psi\ @5000'}=7692\ ACFM\ (wet)$$

c. Flue Gas Concentration. Based on the mass flow rate of HD and the actual stack gas flow, the stack gas concentration is:

$$\frac{\left(0.00255\frac{lb}{hr}\right)\left(4.54\times10^{8}\ \frac{\mu g}{lb}\right)}{\left(7692\frac{ft^3}{\min}\right)\left(60\frac{\min}{hr}\right)\left(0.02832\frac{m^3}{ft^3}\right)}=89.36\frac{\mu g}{m^3}$$

d. Calculation of Collected Sample Mass.

$$\left(89.36\frac{\mu g}{m^3}\right)\left(0.15\frac{L}{\min}\right)(240\ \min)\left(1.0\times10^{-3}\ \frac{m^3}{L}\right)\left(1{,}000\frac{ng}{\mu g}\right)=3217\ ng$$

5. Conclusion. Because the collected sample mass (3217 ng) is greater than the detection limit (72 ng), the sampling and analytical method will be able to demonstrate the 99.99% DRE for the lowest amount of HD to be fed during the Trial Burn.